

Article

Attempts to Obtain Material Based on Polyvinyl Alcohol with Barrier Properties against Water Vapor

Lucica Maria Pop ^{*}, Anca Mihaly Cozmuta, Camelia Nicula , Leonard Mihaly Cozmuta and Anca Peter 

Faculty of Sciences, Technical University of Cluj Napoca, North University Center of Baia Mare, 430122 Baia Mare, Romania; Mihaela.MIHALY@cb.utcluj.com (A.M.C.)

* Correspondence: lucica_pop74@yahoo.it

Abstract: The purpose of this study was to obtain a biodegradable film based on polyvinyl alcohol with reduced water vapor permeability. The hydrophobic character of the films was achieved by incorporating beeswax, vegetable bio-surfactant, citric acid as a cross-linking agent, and glycerol to provide elasticity, along with the application of thermal treatment. Water vapor permeability was determined gravimetrically. The results indicated that all films produced had lower water vapor permeability compared to unmodified or untreated polyvinyl alcohol films. The barrier to water vapor varied directly with the mass of beeswax used, and the homogeneous dispersion of beeswax in the polyvinyl alcohol matrix was essential for achieving an efficient hydrophobic film. The best performing-material exhibited a water vapor permeability 5.15 times lower than that of the neat polyvinyl alcohol and 15 times higher than that of polyethylene. Considering the fact that the water vapor barrier property of neat polyvinyl alcohol was 78 times lower than that of polyethylene, the combination of beeswax, citric acid, and vegetable bio-surfactant—along with thermal treatment—can be a viable solution to reduce the hygroscopicity of polyvinyl alcohol-based films.

Keywords: biodegradability; polyvinyl alcohol; beeswax; water vapor permeability; hygroscopicity; hydrophobicity



Citation: Pop, L.M.; Mihaly Cozmuta, A.; Nicula, C.; Mihaly Cozmuta, L.; Peter, A. Attempts to Obtain Material Based on Polyvinyl Alcohol with Barrier Properties against Water Vapor. *Appl. Sci.* **2024**, *14*, 4310. <https://doi.org/10.3390/app14104310>

Academic Editor: Raffaele Marotta

Received: 12 March 2024

Revised: 15 May 2024

Accepted: 16 May 2024

Published: 19 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The growing concern for environmental pollution and the widespread accumulation of huge amounts of plastic waste, which remains in the environment for a long time and has a negative impact on resource depletion as well as human health, have led many institutions to adopt Sustainable Development Goals to reduce the impact of these materials on the environment. Under the influence of several factors, these plastics break down into very small particles, so-called microplastics (smaller than 5 mm), which can be ingested by animals, birds and marine fauna and pose a threat to all trophic levels [1].

Traditional plastics are used in many industries, with some materials having a longer lifespan, such as those used in construction, lasting about 35 years, and others, like packaging materials, having a shorter lifespan of about 6 months. In contrast, biodegradable materials degrade in shorter periods of time, about 1–2 months, compared to traditional materials that can remain in the environment for centuries or even longer [2].

The current trend is to find viable and environmentally friendly solutions to replace non-degradable petroleum-based plastics with sustainable, renewable, hydrophobic and biodegradable materials that can be recycled and composted. This aims to reduce fossil fuel dependence and greenhouse gas footprint in the environment and promote more efficient use of renewable resources [3,4].

Biodegradable polymeric materials have been the subject of numerous studies due to their unique benefits, such as: excellent film-forming properties, good mechanical, optical and thermal properties, corrosion resistance, low weight and high hardness, and excellent oxygen barrier properties. However, these materials also have some disadvantages, such

as high water vapor permeability (WVP). Despite the efforts of by many researchers, due to these limitations, there are few biodegradable polymers that meet the requirements of modern society's packaging needs [2,5].

There are various studies in the literature on obtaining hydrophobic surfaces for potential packaging materials, but obtaining environmentally friendly and sustainable hydrophobic materials remains a major challenge. The water vapor barrier performance of biomaterials can be influenced by various factors such as sample preparation methods (casting, biaxial orientation, annealing), test conditions (temperature, humidity), and micro-morphology (crystallization, phase separation) [6,7]. Under high humidity conditions, the biopolymer matrix should be cross-linked to ensure the integrity. Cross-linking refers to the reactions that lead to the formation of bonds between polymer chains [8].

Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer widely studied by researchers. It is applicable in many industries, such as: biomedicine, cosmetics, and pharmaceutical industry, in the paper, textile, and paint industries, in construction. Recently, there has been growing interest in obtaining packaging biomaterials for use in the food industry, either as a film [9], as a layer in biocomposites, or as a coating [10].

PVA can be completely broken down by appropriately acclimatized microorganisms [11]. Its biodegradation can occur under aerobic or anaerobic conditions. Under appropriate environmental conditions (pH and temperature), selected microorganisms grow rapidly, resulting in the rapid degradation of the polymer. This process should be completed in a minimum of 6 and a maximum of 12 weeks [12]. The biodegradability of PVA has been demonstrated since the early 1930s. Biodegradation occurs through hydrolysis or enzymatic cleavage of the polymer matrix [1,13].

PVA is one of the most commonly used biopolymers for the production of bioplastics. It is a biodegradable synthetic polymer obtained by the hydrolysis of poly(vinyl acetate) under alkaline conditions [14]. PVA is non-toxic, water-soluble, exhibits excellent biocompatibility, and good mechanical and thermal properties [15]. It is easy to process, highly polar, and forms strong hydrogen bonds in the presence of hydroxyl groups. Although it has low oxygen permeability [16] it exhibits high WVP.

Reducing the WVP of PVA-based films can be achieved by combining the biopolymer with other materials [17], adding multiple functional constituents [18,19] such as cross-linking agents or plasticizers [20], or applying various methods such as grafting, etherification, phosphorylation, acetylation, freezing, heat treatment, or irradiation [21,22].

The transfer of water between food and the environment influences the shelf life of food leading to its alteration. For this reason, many researchers have devoted their attention to improving this barrier property by mixing PVA with other biopolymers or using various chemical or physical methods [23]. A packaging material with a low permeability prevents water from penetrating the food, thus preventing the growth of microorganisms on or within its surface [24]. Hydrophobic films and coatings can reduce the rate of water molecule transfer acting as effective barriers against moisture. Mixing waxes into the polymer matrix can also be a viable strategy for improving water vapor barrier properties due to their hydrophobic character. The type and amount of wax and emulsifiers, as well as different preparation conditions (such as temperature and homogenization conditions) are important factors that influence the stability, structure, and properties of the film. For a more homogeneous dispersion of wax in the film matrix, its melting point should be as low as possible helping to obtain small droplets facilitating the formation of emulsion. Cheng et al. [25] tested three types of wax (beeswax (BW), candelilla wax (CL), and carnauba wax (CB)) for reducing the hydrophilicity of edible starch/gelatin films prepared by extrusion blowing. By incorporating BW and CL into the matrix, the film surface became rougher and more irregular, thus improving the surface hydrophobicity of the film. Films containing BW showed the stronger thermal stability and the lowest permeability to water vapor. The authors of this study recommended BW for obtaining edible films with low water vapor permeability.

BW is commonly used to produce hydrophobic films or coatings. It has a complex composition, containing various constituents including long-chain hydrocarbons, fatty acids, free acids and esters, alcohols. Beeswax has a melting point of 63–65 °C, is insoluble in water, and has a yellowish color. The superhydrophobic nature of BW is attributed to the methylene [int-(CH₂)] carbons in the internal chain of which more than 95% is present [26]. Zhang et al. [27] prepared agar/maltodextrin-beeswax (A/M-BW) pseudo-bilayer films and studied drying temperatures and homogenization conditions to increase the hydrophobicity of the films. The best results were obtained at 80 °C and 8000 rpm for 1 min. Composite films based on PVA/polyacrylic acid (PAA) were prepared by Lim et al. [28] who studied the effect of wax content on the formation of solutions. The analysis results showed that excessive wax content led to the separation of solution phases, resulting in non-homogeneous structures due to the clumping of BW. The best results were achieved with a film containing 10% BW, which improved the properties against water, oxygen and oil.

Emulsifiers are amphiphilic substances that determine the interaction between lipids and matrices and contribute to their homogeneous dispersion in the film matrix. They can reduce the size of droplets in the emulsion thus increasing the number of drops in it [29]. Tanwar et al. [30] prepared PVA and starch films, then added coconut shell extract (CSE) in different mass proportions (3, 5, 10, and 20%) and sepiolite clay to obtain a material with antioxidant properties for food packaging. The mechanical and thermal properties of the films improved by adding CSE and sepiolite clay to the matrix due to the formed hydrogen bonds. Phenolic extent in films varied in direct proportion to the amount of CSE. Water vapor permeability and the antioxidant activity of films have also been improved with the addition of CSE to the film matrix. Soybean oil packaged in the films obtained showed improved oxidative stability. The authors recommend CSE as an antioxidant, but recommend reducing WVP of packaging films.

Cross-linking agents are also introduced into the film matrix to achieve better conjugation of film components, thereby improving the properties of the films.

In active carboxymethyl cellulose, PVA, and *Aloe Vera* films, Kanatt et al. [31] introduced citric acid as a cross-linking agent and the films obtained were analyzed. The permeability, solubility, and moisture content decreased with the addition of CA and the physical-chemical and mechanical properties of the films improved. The results of the analyses showed that the incorporation of CA led to cross-linking by the formation of ester bonds. The films were tested for minced meat packaging and delayed lipid peroxidation and prevented the growth of microorganisms in minced meat.

Additionally, Musetti et al. [23] introduced poly (ethylene glycol) (PEG) and CA into the PVA matrix as cross-linking agents to obtain a thin film carrying antimicrobial agents. Given all the performance CA has demonstrated in forming inter-catenary bounds, it was necessary to include PEG in the film to diminish the film's hydrophilic behavior. The results showed that the developed matrix could be a promising material for the incorporation of active ingredients.

Thermal treatment is another method used and mentioned in the literature to improve the water vapor barrier properties of PVA-based film. Bellelli et al. [32] used CA and malic acid to improve the properties of PVA films. The addition of acids combined with heat treatment gave them double effect, namely, cross-linking and plasticizing. The results of this study showed improved mechanical resistance of the films and WVP was reduced by applying heat treatment and even more with the addition of acids. Film transparency was not affected by heat treatment, but when coupled with the addition of acids it resulted in slight yellowing.

The aim of this study was to find a suitable strategy to improve the WVP of the PVA-based biodegradable polymer, through physical or chemical modifications or a new design of the polymer structure using organic compounds to minimize the environmental impact. This would allow it to be used as a potential packaging material even in wet or aqueous environments. The study also investigated the effect of thermal curing on the obtained

films. The heat treatment applied to the biomaterials were at 125 °C and 150 °C. At the end of the study, by comparing the results obtained, it was determined which formula is optimal for improving the performance of PVA-based films, in terms of WVP.

In this preliminary study, the goal was to develop a series of PVA-based materials that exhibit good water vapor barrier properties, in order to obtain a biodegradable material that could replace non-degradable materials and could potentially be used as food packaging material. The biodegradable character of PVA and all the materials used to obtain the films from this study is already known from the literature, and the working strategy is like the films obtained, with the best characteristics regarding the water vapor barrier, they will be subsequently selected and subjected to detailed analysis that will include biodegradability, structure, morphology, thermogravimetric analysis, and mechanical properties.

According to our research, there have been no previous studies on PVA-based biomaterials modified with beeswax and vegetable bio-surfactant to improve the water vapor barrier properties of the biomaterial.

2. Materials and Methods

2.1. Materials

Poly(vinyl alcohol) Mowiol[®] 28–99, $M_w = 145,000 \text{ g}\cdot\text{mol}^{-1}$ was purchased from Sigma-Aldrich[®] (Munich, Germany). Citric acid monohydrate (assay 98%) (CA) and Glycerol for analysis (99%) (Gly) were purchased from MultiLab SRL (Bucuresti, Romania). Beeswax (BW) was provided from a local producer on the Romanian market. Coco-betain vegetable origin surfactant (CBS) was purchased from Elemental SRL (Oradea, Romania). Wild oregano oil with 80% carvacrol (OEO) was provided by Provita Nutrition SRL (Bucuresti, Romania). LDPE transparent polyethylene plastic bags made from virgin granules were purchased from Stifany Impex SRL (Bucuresti, Romania).

2.2. Film Preparation

The solution casting method was used to prepare all films.

Films based on PVA (5 wt%) with the addition of CA, in a ratio of 0.75%, were obtained by placing PVA granules and CA granules in a Berzelius glass over which distilled water was added. The covered beaker heated in a water bath, on a magnetic stirrer, at 80 °C, for approximately 3 h at 500 rotations per minute (rpm) until the granules were completely dissolved and a homogeneous mixture was obtained. Then Gly (1.5 wt%) was added and homogenized for another 5 min on the magnetic stirrer, and the solution thus obtained was sonicated in a Bandelin Sonorex ultrasonic bath, for another 3 min, for a better dispersion. A volume of 10 mL obtained mixture was introduced in every glass Petri dishes with a diameter of 90 mm and the dishes were placed on a straight plane and allowed to dry for two days at room temperature.

The PVA-based films modified with BW were prepared using the same method, with the difference that PVA and CA granules, along with BW in different mass proportions (0.2 and 0.4 g), were dissolved in CBS (1 wt%), under the same conditions, with Gly being added at the end. OEO was added to this solution at a mass proportion of 0.71% after bring it to 65 °C by continuous stirring to obtain the OEO modified PVA-based film.

To obtain a thinner film, the resulting mixture was divided into two equal parts. A volume of 5 mL was introduced in Petri dishes and allowed to dry in the same conditions. These parts were used for individual analysis or for the preparation of double layer films, which also examined the influence of thickness on film permeability.

The double layer films were obtained by two methods. The first method by hot pressing (200 °C) by bonding the films using Mtechnic heat transfer press, 380 × 380 mm, and the second method by previously pouring the solution of the second film over the first dried film before.

The resulting films were heat treated at 125 °C and 150 °C in a preheated Binder oven for 20 min and all the films obtained can be seen in Table 1.

Table 1. Types of films obtained, the corresponding code, the method of preparation and film thickness.

Film	Film Code	Preparation Method	Film Thickness (mm)
PVA	PVA	PVA was mixed with distilled water and heating on the magnetic stirrer and finally treated with ultrasound.	0.33 ± 0.0094
PVA + 0.75% CA + Gly	PVA I	PVA, CA, and distilled water were mixed and heated on the magnetic stirrer. As the mixture formed, Gly was added and sonicated.	0.33 ± 0.0015
PVA + 0.75% CA + 0.2 g BW + CBS + Gly	PVA II	PVA, CA, and BW were mixed and heated with CBS on magnetic stirrer, and Gly was also added and sonicated.	0.33 ± 0.0085
PVA + 0.75% CA + 0.2 g BW + CBS + Gly (thinner)	PVA III	PVA III film was prepared as PVA II film and the resulting solution was divided into two equal parts and poured into two Petri dishes for dry, resulting in a thinner film.	0.17 ± 0.0039
PVA I + PVA III	PVA IV double layer	A PVA IV film was obtained by hot pressing (200 °C) of PVA I and PVA III films, resulting in a double layer film.	0.5 ± 0.0165
PVA + 0.75% CA + 0.4 g BW + CBS + Gly (thinner)	PVA V	PVA, CA, and BW were dissolved in CBS solution by the same procedure and half of the obtained solution was used for the PVA V film.	0.18 ± 0.0010
PVA + 0.75% CA + 0.4 g BW + CBS + OEO + Gly	PVA VI	OEO was introduced in half of the PVA V solution.	0.18 ± 0.0059
PVA I + PVA V	PVA VII double layer	On top of the dried PVA I film the PVA V film solution was added by casting method.	0.5 ± 0.0116
PVA + 0.4 g BW + CBS (+ 5%) + Gly (thinner)	PVA VIII	PVA and BW were dissolved in 5% more concentrated CBS solution, using the same procedure, and half of the obtained solution was used for the PVA VIII film.	0.18 ± 0.0031
PVA + 0.4 g BW + CBS + Gly (thinner)	PVA IX	PVA IX film is the same as PVA V film without CA.	0.18 ± 0.0034

2.3. Film Thickness

The thickness of the films was determined by manually measuring the film at 5 random points with a micrometer, with the thickness being the arithmetic mean of the values. The thickness of the PE film was 0.033 mm.

2.4. Water Vapour Transmission Rate (WVTR)

The WVTR was determined gravimetrically according to the method described by Sobral et al. [33] adapted to this study. The piece of film was attached of 1 cm/cm cross-sectional plastic vial, containing anhydrous silica gel (~5 g). The assembly was weighed, and then placed in a container with water vapor. The assembly was weighed daily and the water vapor flowing through the test film, expressed as the mass gain, represented the WVTR of the test material (Equation (1)).

$$WVTR = \frac{(m_f - m_0)}{m_0} \cdot 100 \quad (1)$$

where:

m_f —final mass of the trial (g);

m_0 —initial mass of the trial (g).

2.5. Water Vapor Permeability (WVP)

WVP is the amount of water that flows through the material per unit time and per unit area, under constant conditions of relative humidity and temperature, and was maintained throughout the test. The WVP of the prepared films has been calculated according to the formula below (Equation (2)) by multiplying WVTR by the thickness of the material and dividing the result by the area of the test surface multiplied by the time at which the result was obtained and by the water vapor pressure gradient, according to the method described by Sobral et al. [33].

$$WVP \left(\frac{\text{g}}{\text{s}} \cdot \text{m} \cdot \text{Pa} \right) = \frac{w \cdot x}{t \cdot A \cdot \Delta P} \quad (2)$$

where:

w —mass increase due to water vapor absorption by silica gel (g);

x —thickness of material;

t —analysis time (s);

A —contact surface (m²);

ΔP —difference between partial pressure of silica gel atmosphere and distilled water (2652 Pa at 40 °C).

2.6. Structure by Fourier-Transformed Infrared Spectroscopy (FTIR)

FTIR spectra were recorded by using a Perkin Elmer Spectrum BX spectrometer. The wavenumber ranged from 4000 to 600 cm⁻¹. Each FTIR spectrum was the average of 8 replicates. The resolution was 4 cm⁻¹.

2.7. Statistical Analysis

All experiments were conducted in triplicates and the mean and standard deviation were determined, which did not exceed 5%. The degree of statistical significance was determined in Microsoft Excel, using One-Way Anova processing, the Tukey model.

3. Results and Discussion

Various PVA-based films were prepared and modified with BW in different mass ratios and through different procedures which were compared with PVA film and PE film to obtain an optimal formula that had the properties required for a potential packaging material with low WVP. Macroscopic image of films obtained can be seen in Table 2.

Table 2. Macroscopic image of films obtained (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

PVA	PVA I	PVA II
		
PVA III	PVA IV double layer	PVA V
		
PVA VI	PVA VII double layer	PVA VIII
		
PVA IX		
		

3.1. PVA Film

The first film prepared was the PVA film which was used as a reference film for comparison with the other films that were subsequently obtained, modified and heat treated. The film obtained can be seen in Table 2. The PVA film was homogeneous, transparent and was easily detached from the Petri dish, but showed plastic properties and poor elasticity. The film thickness was 0.33 mm. The WVTR of the PVA film can be seen in Figure 1, compared with to that of the PE film.

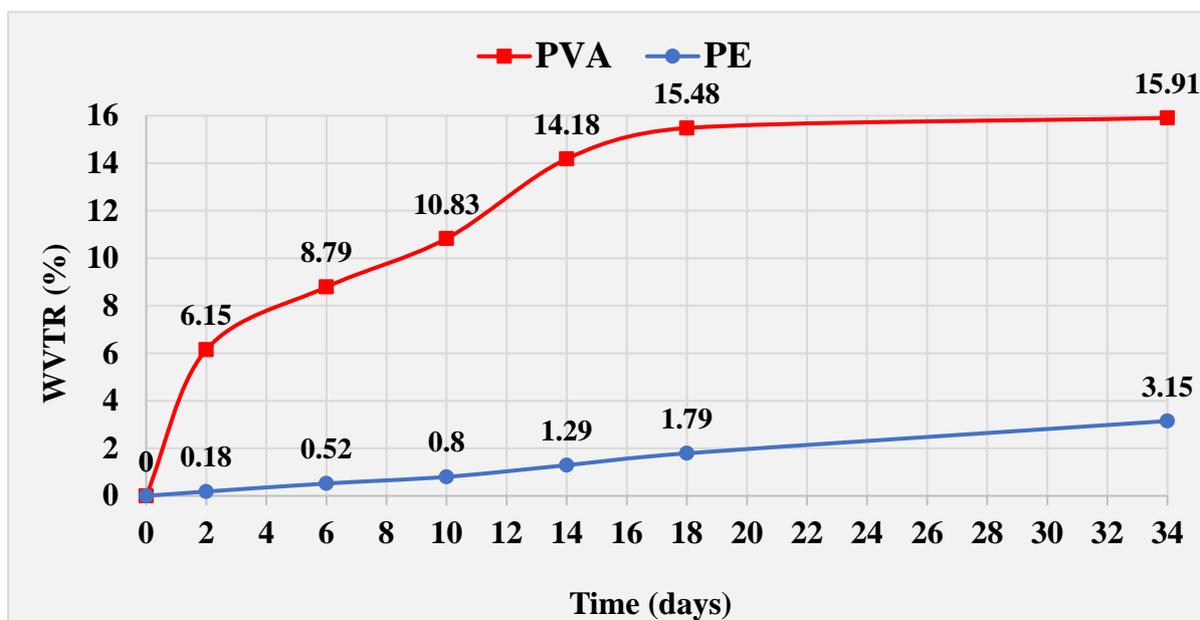


Figure 1. WVTR of PVA and PE films (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

The WVTR of pure PVA film was 5.05 higher than that of the PE film on the 34th, the difference between the two films was 12.76%. Consequently, the PVA film had a higher WVP. The PVA film absorbed the most until the 18th day, then very little after that, while the PE film absorbed evenly over the 34 days. This fact is due to the hydrophilic character of PVA which, in the first phase, absorbs more water vapor, having a higher affinity with water and in the second phase, approaching the saturation state absorbs less, having fewer hydroxyl fractions available [34,35]. The difference between the WVTR values of PVA and PE films is statistically significant at 99% ($p < 0.01$) according to One-Way Anova, the Tukey model.

3.2. PVA Film Modified with 0.75% CA and 1.5% Gly (PVA I)

The PVA I film had a translucent appearance, was well mixed, flexible, and was easily detached from the Petri dish. The thickness of the film was 0.33 mm. The image of the film can be seen in Table 2.

The film was heat treated and the WVTR of the film was determined, which can be seen in Figure 2, compared to that of the pure PVA film and the PE film.

The difference between the untreated PVA I film and the one treated at 125 °C is very small, up to 0.20%. In the first 5 days, the PVA I film shows a higher mass increase, and after 7 days it returns, with the PVA I film treated at 125 °C absorbing more water than the untreated one. Curing the PVA I film at 150 °C is more effective, as the film absorbs less in the first 3 days, 0.67% compared to untreated PVA I film and 0.57% compared to 125 °C, but the effect diminishes and reaches a difference of 0.3% from PVA I film treated at 125 °C and 0.25% from untreated PVA I after 34 days. Compared to untreated and unmodified PVA film, PVA I film has 5.83% lower WVTR compared to untreated heat, 5.78% lower than

that treated at 125 °C and 6.08% lower than film hardened at 150 °C. Compared to PE film, PVA I film has a 6.98% higher WVTR for film cured at 125 °C, 6.93% for untreated film, and 6.68% for film treated at 150 °C. According to the tests carried out, the lowest WVTR was achieved by PVA I film treated at 150 °C. This could be explained by the fact that the effect of CA without heat treatment is only plasticizing, while curing by heat treatment gives CA and cross-linking effect [32], creating as many intermolecular hydrogen bonds as possible between the free -OH fractions of PVA and those of CA, leaving fewer free moieties to interact with water, resulting in a lower WVP of the film and Gly imparts elasticity to the film and increases the mechanical strength of the film, preventing it from breaking after heat treatment [31,36]. The difference between the WVTR values of the modified and heat-treated films and the PVA film is statistically significant at more than 99% ($p < 0.01$) according to One-Way Anova, the Tukey model, which means that the WVP of the PVA film has been improved.

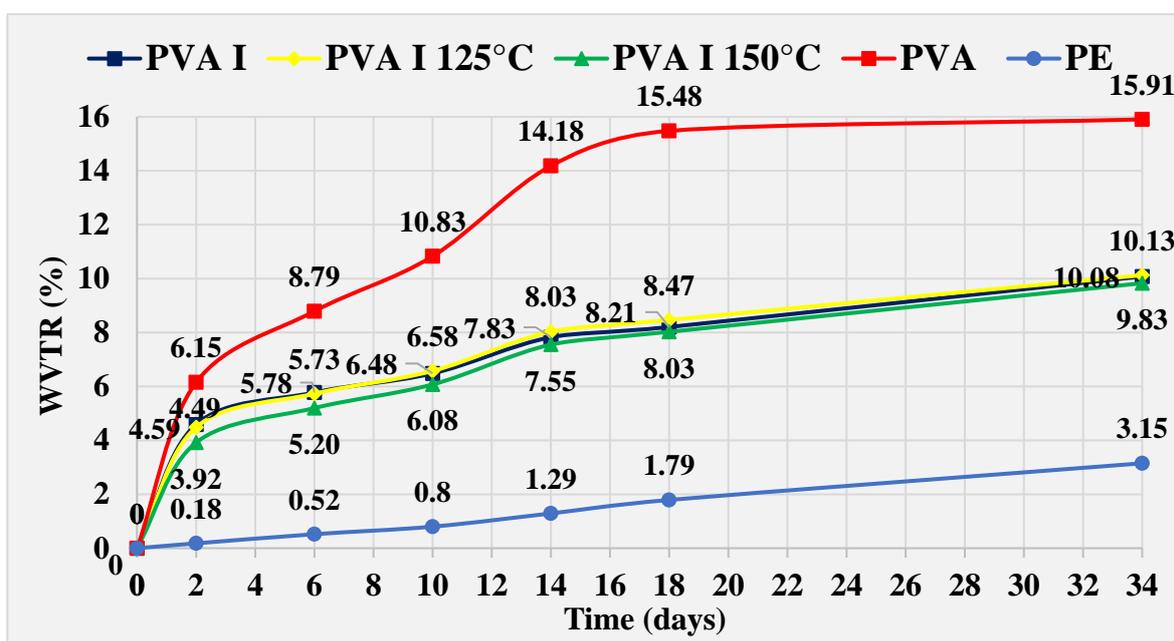


Figure 2. WVTR of untreated PE, PVA, PVA I films and PVA I film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

3.3. PVA Film Modified with 0.75% CA, 0.2 g BW, CBS and Gly 1.5% (PVA II)

The PVA II film is homogeneous, transparent, with a whitish tinge and is easy to peel off from the Petri dish, being 0.33 mm thick. The film can be seen in Table 2.

The film was subjected to heat treatment for curing and the WVTR was recorded, which is shown in Figure 3, compared to that of the PE and untreated PVA film.

The use of heat treatment was effective and improved the water barrier of PVA II films. The best results were achieved with the film treated at 125 °C which had a 0.73% lower WVTR on the first day than the untreated PVA II film. The difference increased to 2.29% on the 8th day and reached 1.1% on the 34th day. When compared to pure PVA film, the PVA II film treated at 125 °C exhibited a decrease in WVTR of 5.78% on day 5, which increased to 6.83% on day 34. Conversely, the pure PVA film showed a 5.73% higher WVTR than the untreated PVA II film. Furthermore, compared to PE film, a PVA II film cured at 125 °C demonstrated a 4.22% higher WVTR on the 13th day, with the difference increasing to 5.93% on the 34th day.

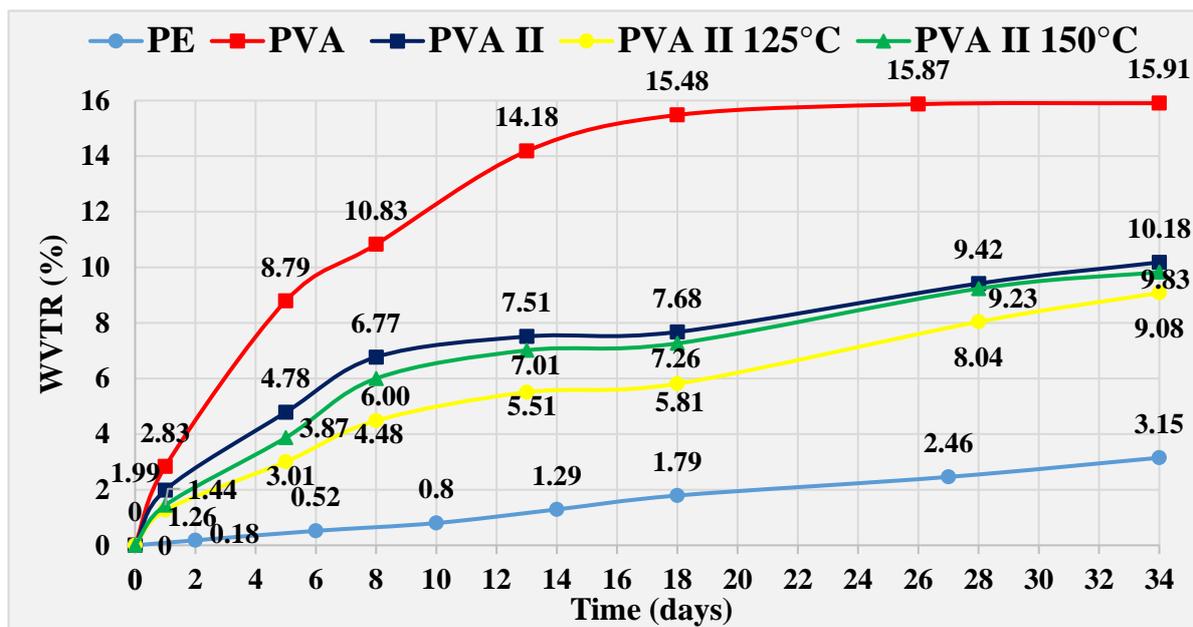


Figure 3. WVTR of untreated PE, PVA, PVA II films, and PVA II film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

These results can be attributed to the hydrophobic character of BW in the film matrix, which reduces water vapor transmission through the matrix, thereby enhancing the film's water barrier properties. BW was found to impart higher hydrophobicity to the film compared to other lipid sources [37,38].

Statistically significant differences of 95% ($p < 0.05$) were recorded between the PVA II film treated at 125 °C and the films PVA II and PVA II treated at 150 °C, respectively, which shows that the film treated at 125 °C has better barrier properties against water vapor. All three films recorded statistically significant differences in proportion of 99% ($p < 0.01$) compared to the PVA film, which means that all films improved the WVP of the PVA film according to One-Way Anova, the Tukey model.

3.4. PVA Film Modified with 0.75% CA, 0.2 g BW, CBS and 1.5% Gly, Thinner (PVA III)

The film was well homogenized, was thin, 0.17 mm thick, easily detached from the Petri dish and was transparent with a slight tinge of white. The image of PVA III can be seen in Table 2. The WVTR values of this thermally treated film can be seen in Figure 4, compared to those of the PE and untreated pure PVA film.

PVA III film treated at 125 °C achieved the best results, with WVTR values 5.8% lower than the pure PVA film after 34 days. The difference from the PE film is 6.96% for the PVA III film cured to 125 °C and 7.56% for the untreated PVA III film on day 34. The 150 °C heat treatment of the PVA III film was not effective, cracks may have appeared during modeling. The measured WVTR was 4.55% lower than the pure PVA and 8.21% higher compared to the PE. The results obtained suggest that obtaining a thinner film reduces the WVTR of PVA III film compared to the untreated PVA film, because the thickness of the film affects the partial equilibrium pressure of water on the inner surface of the film, giving it greater resistance to water transfer, in the case of hydrophilic films [37]. The values obtained with the film treated at 150 °C could be due to microcracks that may have occurred during modeling of the film.

The PVA III film treated at 150 °C recorded statistically significant differences in the proportion of 95% ($p < 0.05$) compared to the PVA III film as WVTR indicating that heat treatment at 150 °C did not improve the WVP of the PVA III film. The difference between the WVTR values of the modified and heat-treated films and the PVA film is statistically

significant at more than 99% ($p < 0.01$) according to One-Way Anova, the Tukey model, which means that the WVP of the PVA film has been improved.

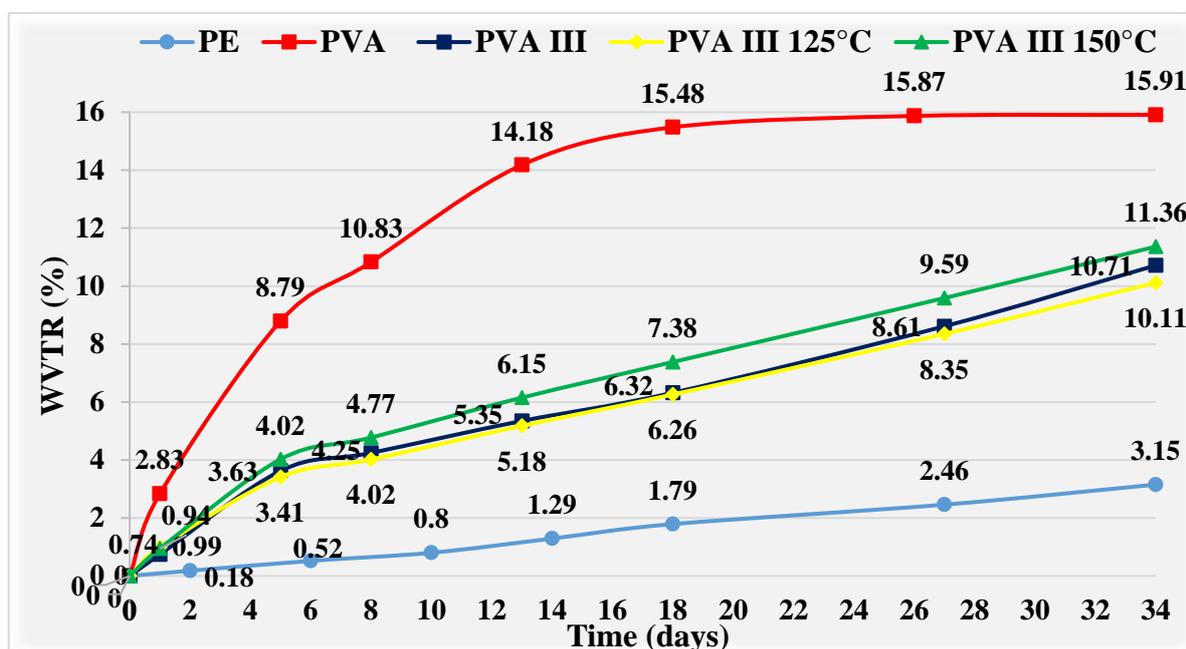


Figure 4. WVTR of untreated PE, PVA, PVA III films, and PVA III film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

3.5. PVA Film Modified with 0.75% CA and 1.5% Gly (PVA I) and PVA Film Modified with 0.75% CA, 0.2 g BW, CBS and 1.5% Gly (PVA III, Thinner) (PVA IV Double Layer)

The films adhered quite well to each other, proving their compatibility, resulting in a fairly transparent film with a slight white tint and a thickness of 0.5 mm. During the heat treatment, the films did not break, but at 150 °C the double layer film yellowed slightly. The image of the film obtained can be seen in Table 2.

The WVTR of the double layer film was calculated and can be seen in Figure 5, compared to that of the PE and pure PVA film.

Heat treatment at 150 °C was not effective on PVA IV film, resulting in values 0.37%, higher than untreated PVA IV film at day 34. However, these are values that 6.77% lower than those achieved with pure PVA film. A PVA IV film cured at 125 °C prevents greater penetration of water through the film compared to an untreated PVA IV film. The difference recorded is 1.29%, and for pure PVA film the difference is 8.43% at day 34. The difference in WVTR values between PVA IV film treated at 125 °C and PE film is 4.33%, in favor of the PE film on the same day.

PVA IV film achieved better results than PVA II and PVA III film. The formula adopted reduces the permeability of PVA film more effectively provides a better barrier to water vapor, which is achieved by the most hydrophobic layer in the double layer film. Compared to the other films, the WVTR values even approach those of PE film.

The obtained results suggest that the formulation of a double layer film could be a viable strategy to reduce the permeability of PVA films. The results are consistent with those of Hernandez-Garcia et al. [39] who prepared double layer films by thermocompression of a starch-based layer (cassava and corn) with another layer of PLA/poly(3-hydroxybutyrate-co-3-hydroxyvalerate). The authors showed that double layer film had much higher barrier properties against water vapor and oxygen compared to monolayer films.

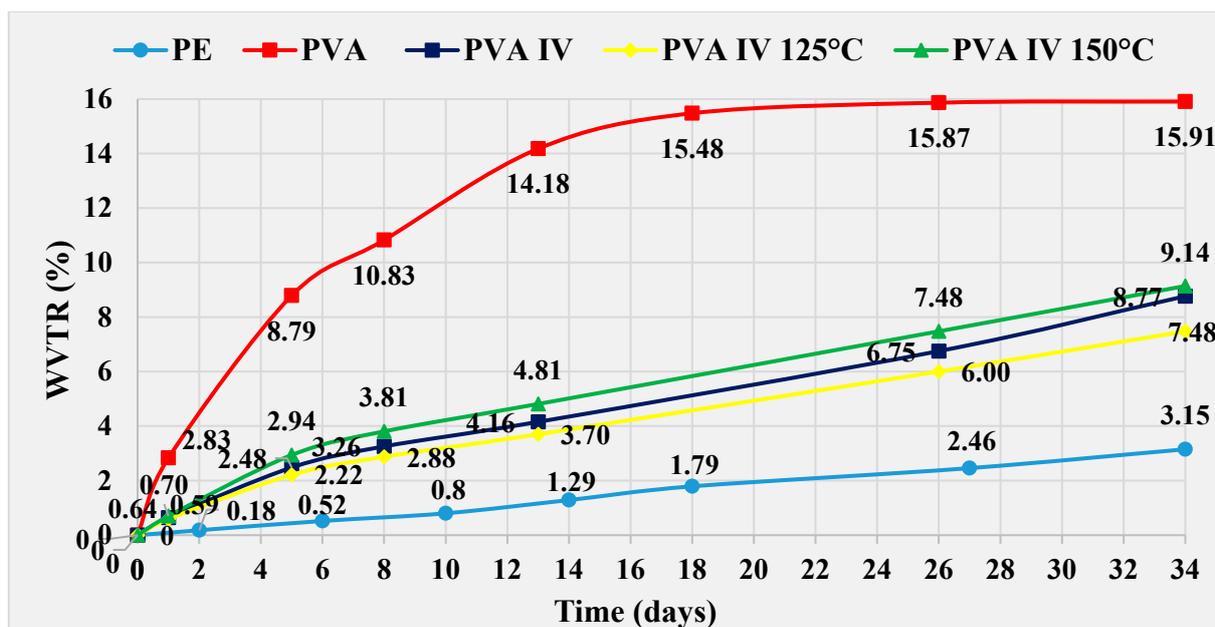


Figure 5. WVTR of untreated PE, PVA, PVA IV films, and PVA IV film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

Statistically significant differences of 95% ($p < 0.05$) in WVTR values were recorded between the PVA IV film treated at 125 °C and the PVA IV and PVA IV films treated at 150 °C respectively, which shows that the film treated at 125 °C has better barrier properties against water vapor. All three films recorded statistically significant differences in proportion of 99% ($p < 0.01$) compared to the PVA film, which means that all films improved the WVT of the PVA film according to One-Way Anova, the Tukey model.

3.6. PVA Film Modified with 0.75% CA, 0.4 g BW, CBS and 1.5% Gly, Thinner (PVA V)

The PVA V film had a homogeneous appearance, the BW was dispersed into very fine particles, there were no wax conglomerates. The film is quite transparent with a whitish hue, it is thin and the heated film showed no cracks and no yellowing. The thickness of the film was 0.18 mm. The image of the film is shown in Table 2 and the WVTR results of the film are shown in Figure 6, compared to those of the PE and pure PVA film.

The best results were obtained by the thermally hardened film at 150 °C, achieving a 1.88% lower WVTR at day 34 compared to the non-heat-treated PVA V film. Compared to the WVTR of the pure PVA film, the WVTR of the film treated at 150 °C is 10.4% lower on the same day, and 2.36% higher compared to the PE film. Heat treatment of the PVA V film at 125 °C was not effective over untreated PVA V film, with the WVTR being 0.23% higher, but the WVTR being 8.29% lower than of pure PVA film and was 4.47% higher than PE film. Untreated PVA V film had WVTR values that were 8.52% lower than pure PVA film and 4.24% higher than PE film.

Increasing the amount of BW combined with heat treatment appears to be an effective strategy to improve the WVP of pure PVA film, because it reduces the moisture content of the films [40]. Similar results were obtained by Pérez-Vergara et al. [37] who prepared edible films based on cassava starch, ethanolic extract of propolis and BW. The researcher reported that the permeability and the moisture of the films obtained varied inversely proportional with the amount of BW.

The PVA V film treated at 150 °C recorded statistically significant differences with regard to WVTR in proportion of 99% ($p < 0.01$) when compared to the PVA V film. This showed that the film treated at 150 °C had better barrier properties against water vapor. The difference between the WVTR values of the modified and heat-treated films and the

PVA film is statistically significant at more than 99% ($p < 0.01$) according to One-Way Anova, the Tukey model, which means that the WVP of the PVA film has been improved.

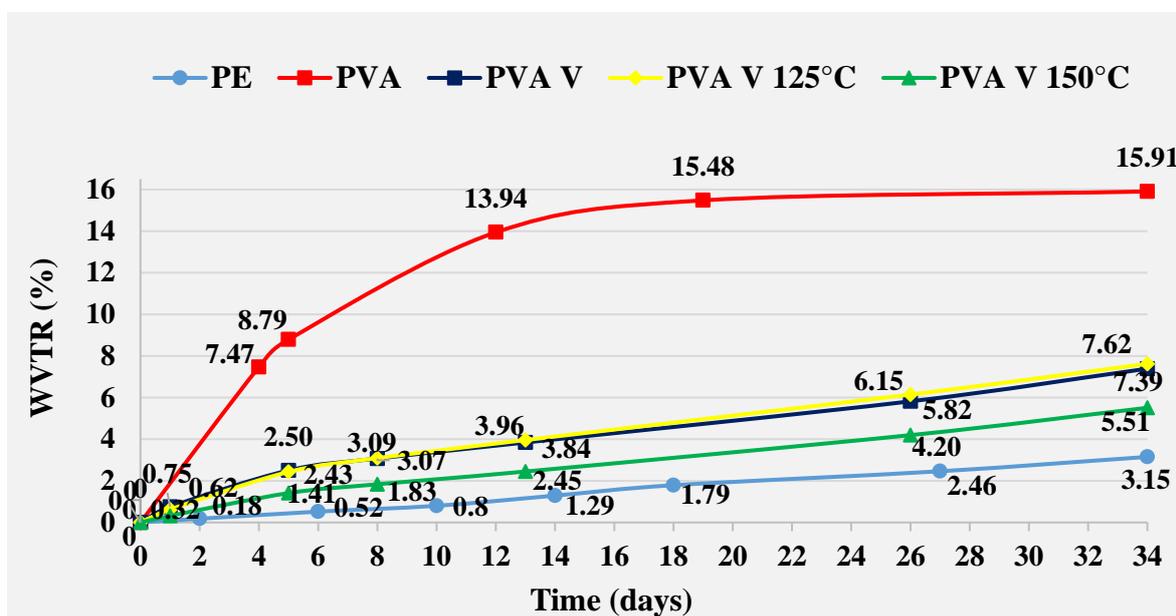


Figure 6. WVTR of untreated PE, PVA, PVA V films and PVA V film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

3.7. PVA Film Modified with 0.75% CA, 0.4 g BW, CBS, 1.5% Gly, and 0.71% OEO, Thinner (PVA VI)

The resulting mixture was not as homogeneous as with the PVA V film, as seen in Table 2, with agglomerations of lipid particles. The film was quite transparent, a slightly whitish, and the thickness of the film was 0.18 mm. The treatment of solution with ultrasounds resulted in particle conglomeration effect. The untreated film had a pleasant oregano smell, which was lost during heat treatment as essential oils had been shown to evaporate at high temperatures [41,42]. However, this was added to the film with the intention of trapping part of it in the matrix network, thereby reducing the WVP of the film. The PVA VI film treated at 150 °C cracked during modeling and the WVTR of the film could not be determined. The WVTR values of the PVA VI film are shown in Figure 7, compared to those of the PE and pure PVA film.

The best results were achieved with a PVA VI film heat treated at 125 °C, which had the lowest WVTR values, 0.74%, on day 34, compared to not thermally hardened PVA VI film, and to pure PVA film, the difference was 8.12%, on the same day. Compared to the PE film, the differences observed were smaller, with the untreated PVA VI film having 5.38% higher WVTR values and the PVA VI film treated at 125 °C showing even smaller differences on day 34, namely 4.64%.

The addition of OEO to the modified BW film can be a good strategy to reduce the permeability of the pure PVA film, since the PVA VI film had almost the same WVTR values as the PVA V film, but possibly a better dispersion of both lipids in the film matrix would lead to even better results.

Increasing the amount of added lipids to reduce the hygroscopicity of films was also confirmed by Reis et al. [40] in their study by preparing trays made of thermoplastic starch materials (TPS) and PLA, obtained by extrusion and thermopressing, which covered with BW emulsion in different mass proportions (1, 2, and 3%), to lower their WVP. The authors demonstrated that the WVP of the trays obtained decreased with increasing the amount of wax from 7.9×10^{-11} to 0.2×10^{-11} g/m \cdot s \cdot Pa due to the hydrophobicity of BW. Zhang

et al. [27] also state that the aggregation and crystallization of BW during drying results in a rougher surface and subsequently in low WVP of the film.

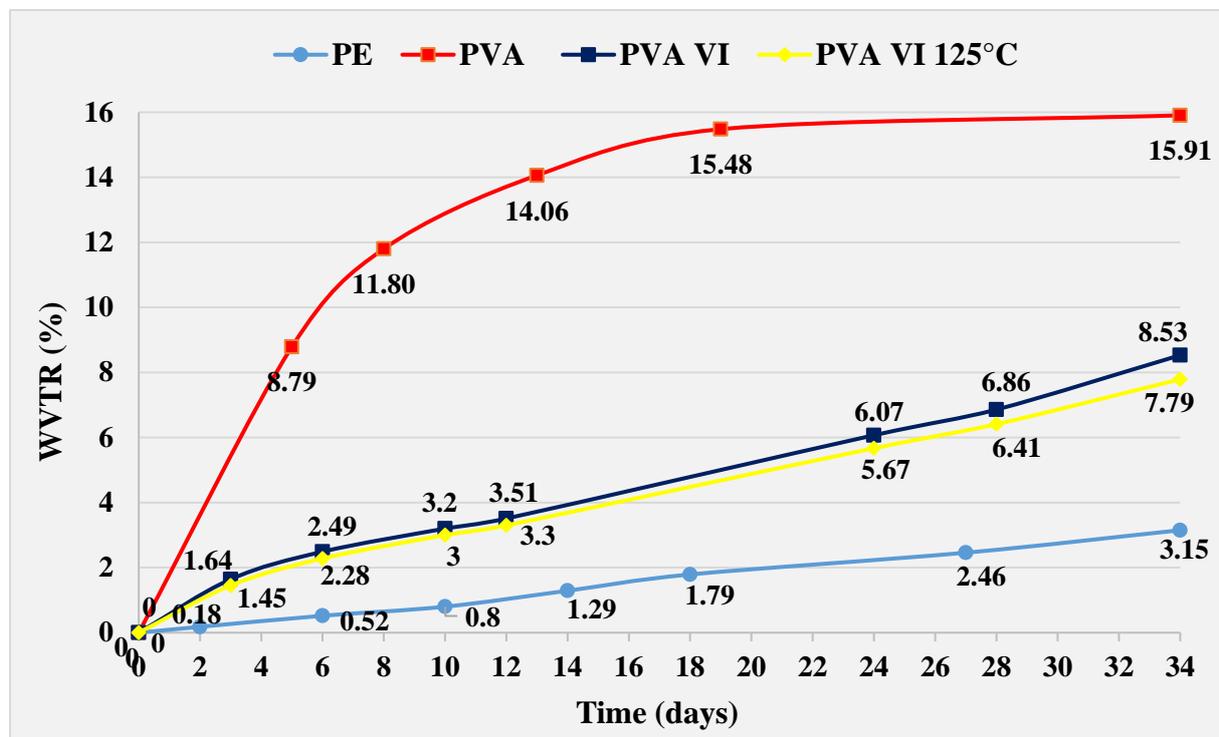


Figure 7. WVTR of untreated PE, PVA, PVA VI films and PVA VI film heat treated at 125 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

The difference between the WVTR values of the modified and heat-treated films and the PVA film is statistically significant at more than 99% ($p < 0.01$) according to One-Way Anova, the Tukey model, which means that the WVP of the PVA film has been improved.

3.8. PVA Film Modified with 0.75% CA and 1.5% Gly (PVA I) and PVA Film Modified with 0.75% CA, 0.4 g BW, CBS and 1.5% Gly (PVA V) (PVA VII Double Layer)

The PVA VII double layer film is well homogenized, with glossy and transparent side and the other side slightly whitish, the combined biomaterials being compatible and making a very good grip. The thickness of the film was 0.5 mm and its image can be seen in Table 2. The WVTR values of PVA VII film subjected to heat treatment are shown in Figure 8 compared to those of the pure PVA film and the PE film.

The heat-treated double-layer film became slightly stiffer and thicker, but did not break, while the film cured at 150 °C turned slightly yellow.

Heat treatment of the double layer PVA VII film at 125 °C was found to be ineffective and gave WVTR values approximately equivalent to those of the untreated PVA VII film; however, compared to pure PVA, the WVTR was reduced by 5.57%. The PVA VII film cured at 150 °C was effective and reduced the WVTR of untreated double layer film by 1.36% on the 26th day and by 1.06% on the 34th day. The untreated PVA VII film had a 5.7% lower WVTR than pure PVA film at day 34, and the 150 °C cured film had 6.76% lower WVTR, reducing the water barrier of the pure PVA film. Compared to the PE film, the WVTR of the double layer film treated at 150 °C was 6% higher, and that of the PVA VII uncured film was 7.06% higher at day 34.

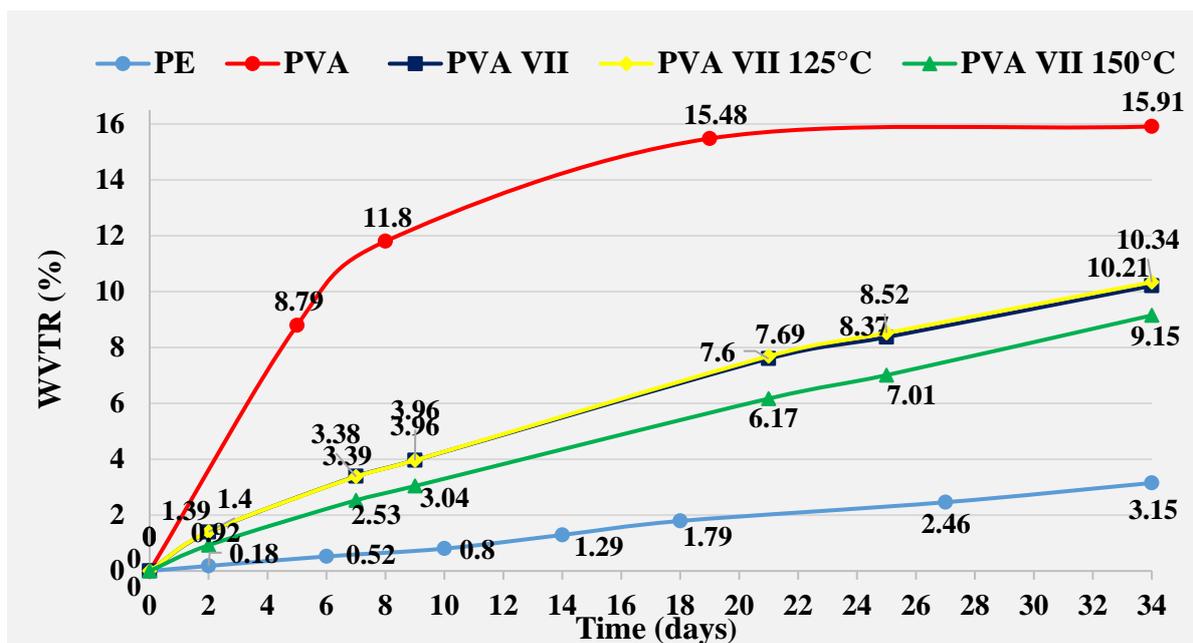


Figure 8. WVTR of untreated PE, PVA, PVA VII films, and PVA VII film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

Double layer films offer better protection against water than monolayers because the permeability of the film is ensured by the layer having higher barrier properties. The results obtained are consistent with a previous study by Zhang et al. [43] who prepared double layer films of chitosan and zein, in different mass proportions, by the casting method. First, the chitosan film was prepared and then dried. The zein film was poured over chitosan film to improve the water barrier properties of chitosan. The authors argue that the desired physico-chemical properties can be achieved depending on the composition of the double layer. The double layer films they obtained showed excellent water vapor barrier properties, and the film containing chitosan-zein at a ratio of 1:3 achieved the best results.

Statistically significant WVTR differences of 99% ($p < 0.01$) were recorded between the treated PVA VII film at 150 °C and the PVA VII film respectively, which means this film improved the WVP of the PVA VII film. Additionally, the difference between the WVTR values of the modified and heat-treated films and the PVA film is statistically significant at more than 99% ($p < 0.01$) according to One-Way Anova, the Tukey model, which means that the WVP of the PVA film has been improved.

3.9. PVA Film Modified with 0.4 g BW, CBS (+5%) and 1.5% Gly, Thinner (PVA VIII)

The PVA VIII film was very thin, but less elastic, probably due to the lack of CA, which gives the film elasticity and helps with cross-linking. The film was quite transparent with a whitish tinge, and the thickness of the film was 0.18 mm. The image of film can be seen in Table 2. Figure 9 shows the WVPR values recorded by the PVA VIII film, compared to those of the pure PVA film and the PE film.

The heat treatment proved to be very effective on this film. The 125 °C cured film recorded WVTR values 4.29% lower than the untreated PVA VIII film and the film treated at 150 °C recorded 4.69% lower at day 34. Compared to pure PVA film, untreated PVA VIII film had 5.04% lower on the same day, and film treated at 125 °C and 150 °C were 9.33% and 9.73% lower, respectively. Compared to the PE film, the values of the treated films are slightly higher, namely, 3.43% for the film treated at 125 °C and 3.03% for the film treated at 150 °C at the 34th day.

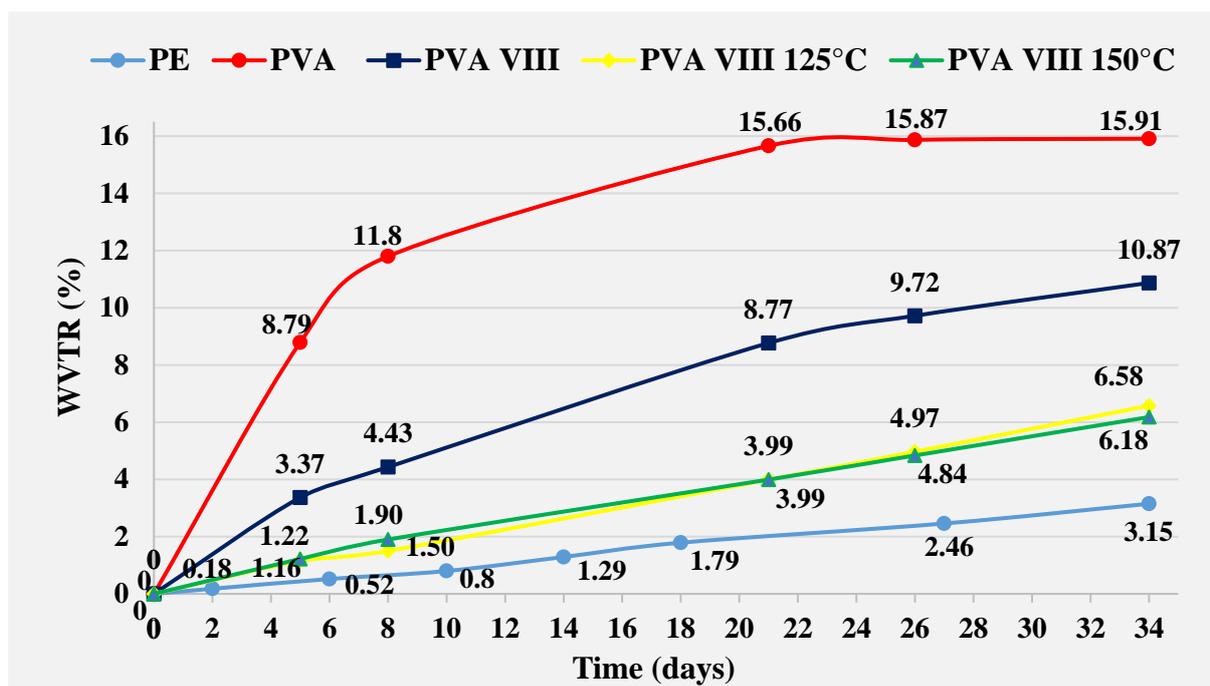


Figure 9. WVTR of untreated PE, PVA, PVA VIII films and PVA VIII film heat treated at 125 °C and 150 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5 %).

The results obtained can be explained by a better dispersion of BW due to the presence of a higher amount of CBS, an emulsifier or surfactant, with amphiphilic character, that is contains both hydrophobic (water-insoluble) and hydrophilic (water-soluble) parts and is absorbed to the interface of the two phases, creating bonds between the phases by reducing the interfacial or surface tensions between them. These results are also confirmed by Zhang et al. [44] who state that the effectiveness of the surfactant is determined by its ability to stabilize emulsions and establish hydrophilic–lipophilic balance (HLB), and a lower HLB value, resulting in a predominantly lipophilic equilibrium in the structure of the molecule, which could prevent water from penetrating into the film matrix.

Statistically significant WVTR differences of 99 % ($p < 0.01$) were recorded between the heat treated films and the PVA VIII film, thus showing the efficiency of heat treatment in improving the WVP of the film. Additionally, the difference between the WVTR values of the modified and heat-treated films and the PVA film is statistically significant at more than 99% ($p < 0.01$) according to One-Way Anova, the Tukey model, which means that the WVP of the PVA film has been improved.

3.10. PVA Film Modified with 0.4 g BW, CBS and 1.5% Gly, Thinner (PVA IX)

Similar to PVA V, the PVA IX film does not contain CA. The films was not very homogeneous, less elastic, quite transparent, slightly whitish, and the thickness of the film was 0.18 mm. The heat treated film did not change color, the film treated at 125 °C bent slightly and could be shaped, but the film cured at 150 °C became stiff and broke when shaping. The image of PVA IX film is shown in Table 2 and the WVTR values are recorded in Figure 10, compared with those of PE film and pure PVA film.

The heat treatment of PVA IX film worked very well and improved the WVTR values of the cured film at 125 °C by 3.36% compared the untreated PVA IX film and achieved 4.03% higher values compared on the 34th day to the PE film. Compared to pure PVA film, the untreated PVA IX film recorded WVTR values 5.37% lower, and PVA IX film treated at 125 °C the values were 8.73% lower on the same day.

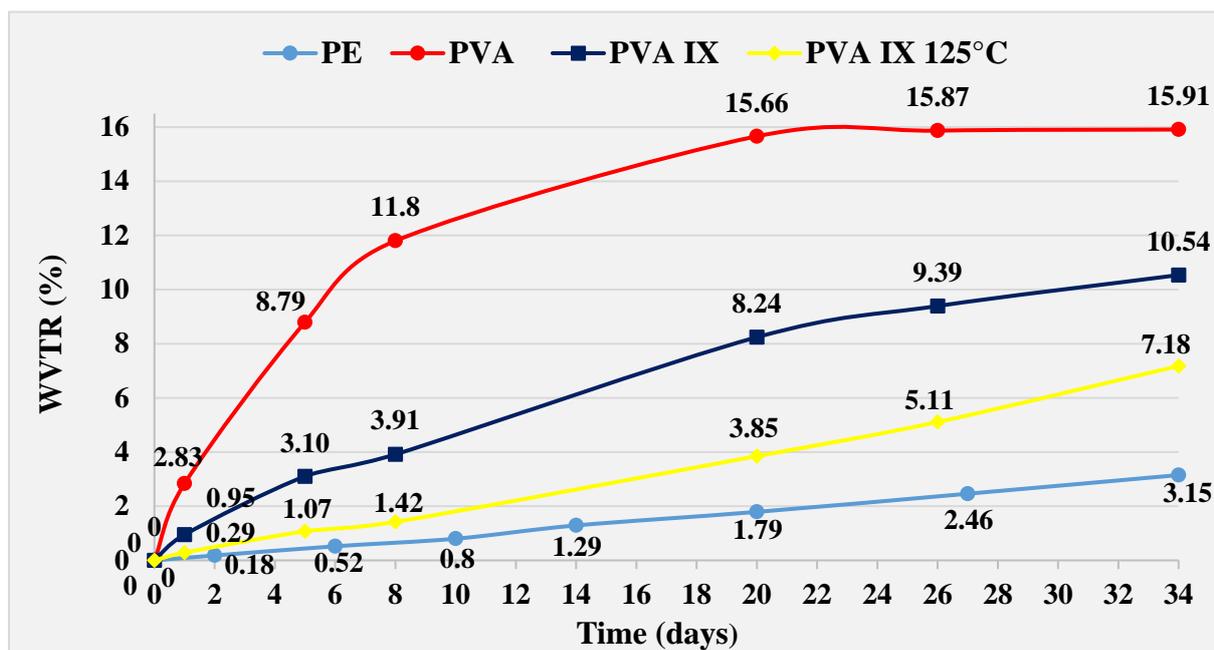


Figure 10. WVTR of untreated PE, PVA, PVA IX films and PVA IX film heat treated at 125 °C (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

These results can be explained by a poor dispersion of BW in the matrix due to the lack of CA, acting as a crosslinking agent, this leads to the creation of a sinuous network by forming hydrogen bonds, preventing the water absorption. This aspect was reported by Wang et al. [45] who prepared modified PVA films with modified xylan and CA to improve the water vapor permeability. First, they modified xylan by (3-mercaptopropyl)trimethoxysilane (MPTMS) and then added it to the solution of PVA and CA as a cross-linking agent. The authors of this study emphasized the importance of the synergistic effect between xylan and CA and the films obtained showed excellent water vapor barriers ($2.79 \times 10^{-13} \text{ g/cm}^{-1} \cdot \text{s} \cdot \text{Pa}$), better than those previously reported.

Statistically significant WVTR differences of 99% ($p < 0.01$) were recorded between all films, meaning that heat treatment improved the WVP of the PVA IX film and both films, PVA IX and PVA IX treated at 125 °C, improved the WVP of the PVA film.

3.11. Structure by Fourier-Transformed Infrared Spectroscopy (FTIR)

Figure 11 illustrates the FTIR spectra of the BW-PVA composite films. The signals from 3293 cm^{-1} correspond to the vibration of OH groups [46] and are present in all PVA based films but not in the FTIR spectrum of the BW, as a result of its hydrophobic property. A weaker signal from the BW-containing films indicates a weakening of the hydrogen bonds of the PVA film due to better matrix conjugation through the presence of BW. The signals from 2915 and 2847 cm^{-1} are assigned to the vibration of methylene groups and are stronger in BW FTIR spectrum than in those of the PVA-based films [46]. The peak at 1736 cm^{-1} is assigned by the vibration of C=O bonds in functional groups from beeswax and appears in the FTIR spectrum of the BW and in those of the PVA-BW films and is absent in the FTIR spectrum of PVA and PVA I [47]. The signals at 1646 cm^{-1} , 1423 cm^{-1} , 1329 cm^{-1} , 1094 cm^{-1} , 1042 cm^{-1} , 922 cm^{-1} , and 825 cm^{-1} appears in the FTIR spectra of PVA and PVA based films and are assigned due to the vibration of C-O/C-H and C-O bonds from alcoholic groups [46]. The peaks in the region $1473\text{--}1175 \text{ cm}^{-1}$ appear in the spectra of BW and of PVA modified with BW. This demonstrates the chemical modification of the PVA-BW structures. By comparing the FTIR spectra of PVA VIII, PVA VIII 125 °C, and PVA VIII 150 °C, common peaks can be observed at 1735 cm^{-1} assigned by the vibration of

C=O bonds, in the region of $1416\text{--}1174\text{ cm}^{-1}$ and at 719 cm^{-1} due to the vibration of the C-O bond in carboxyl groups from free fatty acids [47]. The difference between the FTIR spectra of these samples consists in a weaker signal in the heat treated samples, which is explained by a more intense cross-linking of the network, resulting in a more compacted structure [48].

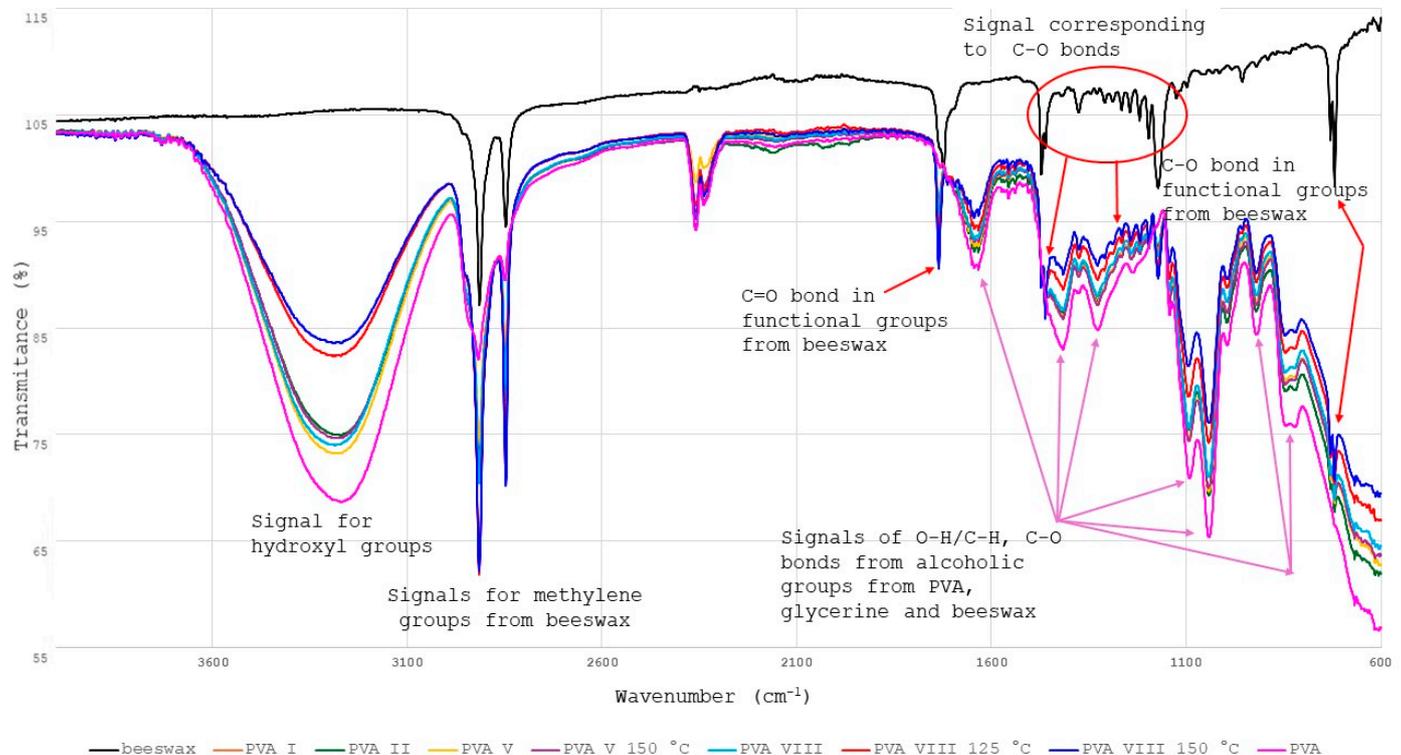


Figure 11. FTIR spectra of the films.

3.12. Water Vapor Permeability (WVP) of the Films

The WVP of the prepared films was calculated using the formula in Section 2.5 (Equation (2)) and the results obtained were compared with the WVP values obtained by the untreated and unmodified PVA film and the PE film. These can be seen in Table 3.

The WVP of untreated and unmodified PVA film was improved by all formulations used in this study.

The best results were obtained with the heat treated PVA VIII film at $150\text{ }^{\circ}\text{C}$, which reduced the WVP of the unmodified and untreated PVA film from $3.92 \times 10^{-10}\text{ g/s}\cdot\text{m}\cdot\text{Pa}$ to $0.76 \times 10^{-10}\text{ g/s}\cdot\text{m}\cdot\text{Pa}$. This film achieved WVP values 5.15 times lower than PVA's.

Compared to the PE film, the best results were achieved with the same film, whose WVP value was $0.71 \times 10^{-10}\text{ g/s}\cdot\text{m}\cdot\text{Pa}$ higher, and with the PVA V film treated at $150\text{ }^{\circ}\text{C}$, which was $0.72 \times 10^{-10}\text{ g/s}\cdot\text{m}\cdot\text{Pa}$ higher than the PE film. WVP values close to those of the PE film are also measured from the thermally treated PVA VIII film at $125\text{ }^{\circ}\text{C}$, which had a WVP $0.79 \times 10^{-10}\text{ g/s}\cdot\text{m}\cdot\text{Pa}$ higher than the PE film, and from the PVA IX film treated to $125\text{ }^{\circ}\text{C}$ whose WVP values were $0.9 \times 10^{-10}\text{ g/s}\cdot\text{m}\cdot\text{Pa}$ higher than the values recorded by the PE film. The WVP of the best performing film is 15 times higher than PE's, while untreated PVA film is 78 times higher than of PE's.

Table 3. WVP of the obtained PVA-based films (the results were obtained in triplicate. The average of the three determinations was reported, with a maximum error of 5%).

Film	Film Code	Water Vapor Permeability (WVP) (g/s·m·Pa) × 10 ⁻¹⁰		
		Untreated	Treated at 125 °C	Treated at 150 °C
PVA	PVA	3.92 ± 0.11%	-	-
PE	PE	0.05 ± 0.03%	-	-
PVA + 0.75% CA + Gly	PVA I	2.01 ± 0.57%	1.87 ± 0.13%	1.90 ± 0.56%
PVA + 0.75% CA + 0.2 g BW + CBS + Gly	PVA II	2.18 ± 0.03%	2.02 ± 0.06%	2.01 ± 0.1%
PVA + 0.75% CA + 0.2 g BW + CBS + Gly (thinner)	PVA III	1.39 ± 0.1%	1.31 ± 0.07%	1.35 ± 0.09%
PVA I + PVA III	PVA IV Double layer	3.18 ± 0.13%	2.81 ± 0.11%	3.29 ± 0.14%
PVA + 0.75% CA + 0.4 g BW + CBS + Gly	PVA V	1.06 ± 0.06%	1.18 ± 0.02%	0.77 ± 0.04%
PVA + 0.75% CA + 0.4 g BW + CBS + EO + Gly	PVA VI	1.21 ± 0.09%	1.07 ± 0.13%	-
PVA I + PVA V	PVA VII Double layer	3.78 ± 0.9%	3.67 ± 0.4%	3.33 ± 0.5%
PVA + 0.4 g BW + CBS (+ 5%) + Gly	PVA VIII	1.32 ± 0.10%	0.84 ± 0.05%	0.76 ± 0.04%
PVA + 0.4 g BW + CBS + Gly	PVA IX	1.29 ± 0.07%	0.95 ± 0.10%	-

4. Conclusions

The WVP of the PVA-based film was improved by all applied formulas. Using the BW to reduce the hygroscopicity of the PVA film could be a viable strategy for obtaining a potential packaging material. The WVP of BW-modified PVA-based films varies inversely with the increase in BW percentage. Films containing BW in a mass ratio of 0.4 g and heat treatment showed the lowest values of WVP, the best value being 0.76×10^{-10} g/s·m·Pa recorded by the film which contained 5% more surfactant.

Obtaining the thinnest possible PVA-based biomaterial, containing BW can be an effective solution to improve the barrier properties against water vapor. The results obtained showed that WVP varies proportionately with the thickness of the film.

Homogeneous dispersion of BW in the PVA film matrix is essential for achieving low water permeability. The WVP of the best performing film is 15 times higher than that of the PE film and 5.15 times lower than that of untreated PVA film, while WVP of untreated PVA film is 78 times higher than that of PE film.

PVA-based film modified with 0.4 g of BW and 5% more CSB was selected to be analyzed in further studies as potential packaging material for food with a high degree of humidity.

Author Contributions: Conceptualization, L.M.P. and A.P.; methodology, L.M.P., A.P., software, L.M.P., validation, A.M.C., C.N., L.M.C. and A.P.; investigation, A.M.C. and A.P.; writing—original draft, L.M.P.; visualization, A.M.C., C.N., L.M.C. and A.P.; supervision, A.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The analyses were conducted at the Research Center for Quality Control and Environmental and Product Safety, within the Department of Chemistry and Biology, Technical University of Cluj-Napoca.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Alonso-López, O.; López-Ibáñez, S.; Beiras, R. Assessment of Toxicity and Biodegradability of Poly(vinyl alcohol)-Based Materials in Marine Water. *Polymer* **2021**, *13*, 3742. [[CrossRef](#)] [[PubMed](#)]
2. Wu, F.; Mirsa, M.; Mohanty, A.K. Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging. *Prog. Polym. Sci.* **2021**, *117*, 101395. [[CrossRef](#)]
3. Chen, Q.; Chang, C.; Zhang, L. Surface engineering of cellulose film with myristic acid for high strength, self-cleaning and biodegradable packaging materials. *Carbohydr. Polym.* **2021**, *269*, 118315. [[CrossRef](#)]
4. Ghaderi, J.; Hosseini, S.F.; Keyvani, N.; Gómez-Guillén, M.C. Polymer Blending Effects on the Physicochemical and Structural Features of the Chitosan/poly(vinyl Alcohol)/fish Gelatin Ternary Biodegradable Films. *Food Hydrocoll.* **2019**, *95*, 122–132. [[CrossRef](#)]
5. Zhang, M.; Biesold, G.M.; Choi, W.; Yu, J.S.; Deng, Y.; Silvestre, C.; Lin, Z. Recent Advances in Polymers and Polymer Composites for Food Packaging. *Mater. Today (Kidlington)* **2022**, *53*, 134–161. [[CrossRef](#)]
6. Li, Y.; Chen, Y.; Wu, Q.; Huang, J.; Zhao, Y.; Li, Q.; Wang, S. Improved Hydrophobic, UV Barrier and Antibacterial Properties of Multifunctional PVA Nanocomposite Films Reinforced with Modified Lignin Contained Cellulose Nanofibers. *Int. J. Biol. Macromol.* **2022**, *14*, 551–558. [[CrossRef](#)] [[PubMed](#)]
7. Xu, J.; Ren, L.; Song, W.; Wu, N.; Zeng, R. Homogeneous Pva/sodium Lignosulfonate Mulch Films with Improved Mechanical and Uv/water Vapor Barrier Properties. *Int. J. Biol. Macromol.* **2024**, *209*, 117975. [[CrossRef](#)]
8. Bueno, J.N.N.; Corradini, E.; Souza, P.R.; Marques, V.d.S.; Radovanovic, E.; Muniz, E.C.; Muniz, E.C.; Muniz, E.C. Films Based on Mixtures of Zein, Chitosan, and PVA: Development with Perspectives for Food Packaging Application. *Polym. Test.* **2021**, *101*, 107279. [[CrossRef](#)]
9. Wu, Y.; Ying, Y.; Liu, Y.; Zhang, H.; Huang, J. Preparation of Chitosan/poly Vinyl Alcohol Films and Their Inhibition of Biofilm Formation Against *Pseudomonas Aeruginosa* PAO1. *Int. J. Biol. Macromol.* **2018**, *118*, 2131–2137. [[CrossRef](#)]
10. Barros-Velazquez, J. Packaging Material in the Food Industry. In *Antimicrobial Food Packaging*; Academic Press: Cambridge, MA, USA, 2006; pp. 97–101.
11. Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. Biodegradation of Poly(vinyl Alcohol) Based Materials. *Prog. Polym. Sci.* **2003**, *28*, 963–1014. [[CrossRef](#)]
12. Singh, R.; Kumar, N.; Mehrotra, T.; Bisaria, K.; Sinha, S. Environmental Hazards and Biodegradation of Plastic Waste: Challenges and Future Prospects. *Bioremediat. Environ. Sustain.* **2021**, *9*, 193–214. [[CrossRef](#)]
13. Chiellini, E.; Corti, A.; Solaro, R. Biodegradation of Poly(vinyl Alcohol) Based Blown Films Under Different Environmental Conditions. *Polym. Degrad. Stab.* **1999**, *64*, 305–312. [[CrossRef](#)]
14. Hedayati, H.R.; Khorasani, M.; Ahmadi, M.; Ballard, N. Preparation of Well-defined Poly(vinyl Alcohol) by Hydrolysis of Poly(vinyl Acetate) Synthesized by RAFT Suspension Polymerization. *Polym. J.* **2022**, *246*, 124674. [[CrossRef](#)]
15. Salazar-Bravo, P.; Torres-Huerta, A.M.; Domínguez-Crespo, M.A.; Brachetti-Sibaja, S.B.; Licona-Aguilar, Á.I.; Rodríguez-Salazar, A.E.; Willcock, H. Electrospun PVA Membranes Reinforced with Cellulose Nanocrystals and Thermally Reduced Graphene Oxide: Thermal, Mechanical and Uv-protection Properties. *Ind. Crops Prod.* **2023**, *197*, 116614. [[CrossRef](#)]
16. Dai, D.D.; Huang, Y.Q.; Sun, L.; Yeh, J.T.; Yeh, J.T. Oxygen Barrier Properties of Organic Montmorillonite Modified Polyamide 11/poly (vinyl Alcohol) Films. *Polym. Adv. Technol.* **2021**, *32*, 165–172. [[CrossRef](#)]
17. Gao, T.; Yan, L.; Yu, Q.; Lyu, Y.; Dong, W.; Chen, M.; Kaneko, T.; Shi, D. High Transparency, Water Vapor Barrier and Antibacterial Properties of Chitosan/carboxymethyl Glucan/poly(vinyl Alcohol)/nanoparticles Encapsulating Citral Composite Film for Fruit Packaging. *Int. J. Biol. Macromol.* **2024**, *261*, 129755. [[CrossRef](#)]
18. Shahid-ul-Islam; Jaiswal, V.; Butola, B.S.; Majumdar, A. Production of Pva-chitosan Films Using Green Synthesized ZnO Nps Enriched with Dragon Fruit Extract Envisaging Food Packaging Applications. *Int. J. Biol. Macromol.* **2023**, *252*, 126457. [[CrossRef](#)]
19. Oun, A.A.; Shin, G.H.; Rhim, J.-W.; Kim, J.T. Recent Advances in Polyvinyl Alcohol-based Composite Films and Their Applications in Food Packaging. *Food Packag. Shelf Life.* **2022**, *34*, 100991. [[CrossRef](#)]
20. Khalid, F.; Roy, A.S.; Parveen, A.; Castro-Muñoz, R. Fabrication of the Cross-linked Pva/tio2/c Nanocomposite Membrane for Alkaline Direct Methanol Fuel Cells. *Mater. Sci. Eng. B.* **2024**, *299*, 116929. [[CrossRef](#)]
21. Shahbazi, M.; Rajabzadeh, G.; Rafe, A.; Ettelaie, R.; Ahmadi, S.J. The Physico-mechanical and Structural Characteristics of Blend Film of Poly (vinyl Alcohol) with Biodegradable Polymers as Affected by Disorder-to-order Conformational Transition. *Food Hydrocoll.* **2016**, *60*, 393–404. [[CrossRef](#)]
22. Mittal, A.; Garg, S.; Kohli, D.; Maiti, M.; Jana, A.K.; Bajpai, S. Effect of Cross Linking of Pva/starch and Reinforcement of Modified Barley Husk on the Properties of Composite Films. *Carbohydr. Polym.* **2016**, *151*, 926–938. [[CrossRef](#)]
23. Musetti, A.; Paderni, K.; Fabbri, P.; Pulvirenti, A.; Al-Moghazy, M.; Fava, P. Poly(vinyl Alcohol)-based Film Potentially Suitable for Antimicrobial Packaging Applications. *J. Food Sci.* **2014**, *79*, 577–582. [[CrossRef](#)]
24. Patil, S.; Bharimalla, A.K.; Mahapatra, A.; Dhakane-Lad, J.; Arputharaj, A.; Kumar, M.; Raja, A.S.M.; Kambli, N. Effect of Polymer Blending on Mechanical and Barrier Properties of Starch-polyvinyl Alcohol Based Biodegradable Composite Films. *Food Biosci.* **2021**, *44*, 101352. [[CrossRef](#)]

25. Cheng, Y.; Zhai, X.; Wu, Y.; Li, C.D.; Zhang, R.; Sun, C.; Wang, W.; Hou, H. Effects of Natural Wax Types on the Physicochemical Properties of Starch/gelatin Edible Films Fabricated by Extrusion Blowing. *Food Chem.* **2022**, *401*, 134081. [[CrossRef](#)]
26. Hosseini, S.F.; Mousavi, Z.S.; McClements, D.J. Beeswax: A Review on the Recent Progress in the Development of Superhydrophobic Films/coatings and Their Applications in Fruits Preservation. *Food Chem.* **2023**, *424*, 136404. [[CrossRef](#)]
27. Zhang, R.; Wang, W.; Wang, W.; Zhang, H.; Dai, Y.; Dong, H.; Kong, L.; Hou, H. Effects of Preparation Conditions on the Properties of Agar/maltodextrin-beeswax Pseudo-bilayer Films. *Carbohydr. Polym.* **2020**, *236*, 116029. [[CrossRef](#)]
28. Lim, W.S.; Kim, M.H.; Park, H.J.; Lee, M.H. Characterization of Polyvinyl Alcohol (pva)/polyacrylic Acid (PAA) Composite Film-forming Solutions and Resulting Films as Affected by Beeswax Content. *Polym. J.* **2024**, *16*, 310. [[CrossRef](#)]
29. Ortega-Toro, R.; Jiménez, A.; Talens, P.; Chiralt, A. Effect of the Incorporation of Surfactants on the Physical Properties of Corn Starch Films. *Food Hydrocoll.* **2014**, *38*, 66–75. [[CrossRef](#)]
30. Tanwar, R.; Gupta, V.; Kumar, P.; Kumar, A.; Singh, S.; Gaikwad, K.K. Development and Characterization of Pva-starch Incorporated with Coconut Shell Extract and Sepiolite Clay as an Antioxidant Film for Active Food Packaging Applications. *Int. J. Biol. Macromol.* **2021**, *185*, 451–461. [[CrossRef](#)] [[PubMed](#)]
31. Kanatt, S.R.; Makwana, S.H. Development of Active, Water-resistant Carboxymethyl Cellulose-poly Vinyl Alcohol-aloe Vera Packaging Film. *Carbohydr. Polym.* **2020**, *227*, 115303. [[CrossRef](#)] [[PubMed](#)]
32. Bellelli, M.; Licciardello, F.; Pulvirenti, A.; Fava, P. Properties of Poly(vinyl Alcohol) Films as Determined by Thermal Curing and Addition of Polyfunctional Organic Acids. *Food Packag. Shelf Life* **2018**, *18*, 95–100. [[CrossRef](#)]
33. Sobral, P.J.d.A.; Menegalli, F.C.; Hubinger, M.D.; Roques, M.A. Mechanical, Water Vapor Barrier and Thermal Properties of Gelatin Based Edible Films. *Food Hydrocoll.* **2001**, *15*, 432. [[CrossRef](#)]
34. Li, G.; Meng, L.; Wang, J.; Chen, G.; Wu, X.; Su, Q. Water Vapor Permeability in Heterogeneous Porous Membranes: Analytical Modeling and Experimental Characterization. *Int. Commun. Heat Mass Transf.* **2023**, *147*, 106950. [[CrossRef](#)]
35. Kassa, A.; Sekine, R.; Dorji, T.; Pathak, G.K.; Hayano, K.; Yamauchi, H.; Mochizuki, Y. Insights into Water Absorption Characteristics of Various Waste-based Inorganic Additives and Their Application for Soil Stabilization. *J. Clean. Prod.* **2024**, *446*, 141470. [[CrossRef](#)]
36. Ooi, Z.X.; Ismail, H.; Bakar, A.; Aziz, N.A.A. The Comparison Effect of Sorbitol and Glycerol as Plasticizing Agents on the Properties of Biodegradable Polyvinyl Alcohol/rambutan Skin Waste Flour Blends. *Polym. Plast. Technol. Eng.* **2012**, *51*. [[CrossRef](#)]
37. Pérez-Vergara, L.D.; Cifuentes, M.T.; Franco, A.P.; Pérez-Cervera, C.; Andrade-Pizarro, R.D. Development and Characterization of Edible Films Based on Native Cassava Starch, Beeswax, and Propolis. *NFS J.* **2020**, *21*, 39–49. [[CrossRef](#)]
38. Osa, R.; Apaliya, M.T.; Alolga, R.N.; Kwaw, E.; Otu, P.N.Y.; Akaba, S. Influence of Shea Butter, Bee Wax and Cassava Starch Coatings on Enzyme Inactivation, Antioxidant Properties, Phenolic Compounds and Quality Retention of Tomato (*solanum Lycopersicum*) Fruits. *Appl. Food Res.* **2022**, *2*, 100041. [[CrossRef](#)]
39. Hernández-García, E.; Vargas, M.; Chiralt, A. Thermoprocessed Starch-polyester Bilayer Films as Affected by the Addition of Gellan or Xanthan Gum. *Food Hydrocoll.* **2021**, *113*, 106509. [[CrossRef](#)]
40. Reis, M.O.; Olivato, J.B.; Bilck, A.P.; Zanela, J.; Grossmann, M.V.E.; Yamashita, F. Biodegradable Trays of Thermoplastic Starch/poly (lactic Acid) Coated with Beeswax. *Ind. Crops Prod.* **2018**, *112*, 481–487. [[CrossRef](#)]
41. Tampau, A.; González-Martínez, C.; Chiralt, A. Polyvinyl Alcohol-based Materials Encapsulating Carvacrol Obtained by Solvent Casting and Electrospinning. *React. Funct. Polym.* **2020**, *153*, 104603. [[CrossRef](#)]
42. Wang, L.; Heising, J.; Fogliano, V.; Dekker, M. Fat Content and Storage Conditions Are Key Factors on the Partitioning and Activity of Carvacrol in Antimicrobial Packaging. *Food Packag. Shelf Life* **2020**, *24*, 100500. [[CrossRef](#)]
43. Zhang, L.; Li, K.; Yu, D.; Regenstein, J.M.; Dong, J.; Chen, W.; Xia, W. Chitosan/zein Bilayer Films with One-way Water Barrier Characteristic: Physical, Structural and Thermal Properties. *Int. J. Biol. Macromol.* **2022**, *200*, 378–387. [[CrossRef](#)]
44. Zhang, R.; Zhai, X.; Wang, W.; Hou, H. Preparation and Evaluation of Agar/maltodextrin-beeswax Emulsion Films with Various Hydrophilic-lipophilic Balance Emulsifiers. *Food Chem.* **2022**, *384*, 132541. [[CrossRef](#)] [[PubMed](#)]
45. Wang, Y.; Guo, X.; Li, J.; Jia, W.; Qian, F.; Wang, H.; Lv, Y.; Lv, Y. Synergistic Effects of (3-mercaptopropyl)trimethoxysilane and Citric Acid on the Improvement of Water Vapor Barrier Performance of Polyvinyl Alcohol/xylan Packaging Films. *Ind. Crops Prod.* **2021**, *171*, 113822. [[CrossRef](#)]
46. Franca, T.; Goncalves, D.; Cena, C. ATR-FTIR Spectroscopy Combined with Machine Learning for Classification of PVA/PVP Blends in Low Concentration. *Vib. Spectrosc.* **2022**, *120*, 103378. [[CrossRef](#)]
47. Zuber, B.; Cersoy, S.; Herbin, M.; Sablier, M.; Rouchon, V. Beeswax-rosin Mixtures in Historical Wet Collection Sealants: Qualitative Analysis of Their Composition by DSC and ATR-FTIR Spectroscopy. *Vib. Spectrosc.* **2021**, *117*, 103310. [[CrossRef](#)]
48. Tulloch, A.P. Beeswax—Composition and Analysis. *Bee World* **1980**, *61*, 47–62. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.